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(54) Title of the Invention: Moisture-Curable Sealing material composition

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## **Specification**

### **1. Title of the Invention**

Moisture-Curable Sealing Material Composition

### **2. Claims**

1. A moisture-curable sealing material composition comprising a prepolymer mixture consisting of

urethane prepolymer (A) obtained by reacting a polyalkylene ether triol having a molecular weight of 4,000 to 8,000 and excess diphenylmethane-4,4'-diisocyanate, and

urethane prepolymer (B) obtained by reacting a polyalkylene ether diol or polyalkylene ether triol having a molecular weight of 2,000 to 6,000 and excess tolylene diisocyanate,

said moisture-curable sealing material composition characterized in that the mixture ratio by weight of urethane prepolymer (A) and urethane prepolymer (B) is 95:5 to 70:30.

2. The moisture-curable sealing material composition according to claim 1, further characterized in that the polyalkylene ether triol or polyalkylene ether diol in urethane prepolymers (A) and (B) is polypropylene ether triol or polypropylene ether diol wherein the number of ethylene oxide moles added is 20 mol% or less.

### **3. Detailed Description of Invention**

#### **Industrial Field of Use**

The present invention relates to a moisture-curable sealing material composition, and in further detail, to a one-liquid moisture-curable urethane sealing material

composition that is appropriate, for instance, for sealing of automobile frames and provides excellent adhesion with painted surfaces and plastics in particular, even if the open time is 10 minutes or longer, without requiring primer treatment.

### **Prior Art and Problems to Be Solved by the Invention**

One-liquid moisture-curable urethane sealing material compositions are sealing material compositions that cure as a result of reaction between the isocyanate groups in the composition and the water content (moisture) in air, and they have excellent properties.

However, when these sealing material compositions do cure, carbon dioxide gas is generated by the reaction between the isocyanate groups and moisture content. In the case of one-liquid moisture-curable urethane sealing material compositions having a rapid curing rate in particular, carbon dioxide foam tends to be generated within the composition, or near the interface between the composition and the item to be bonded. There is a disadvantage in that this foaming has a negative impact on the sealing effect and strength, and adhesion with the object to be bonded, and this tendency becomes stronger with an increase in temperature and humidity. There is a need for the development of a sealing material composition that does not pose this disadvantage.

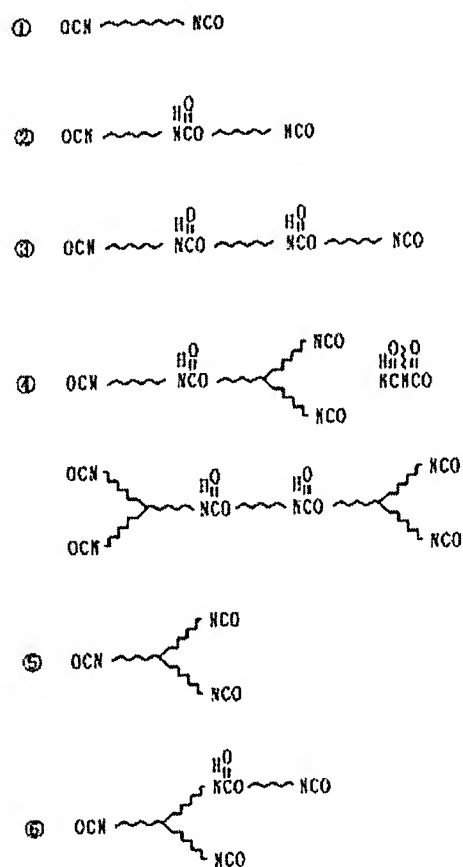
It has been proposed, for instance, that a one-liquid moisture-curable urethane sealing material composition be used to attach an automobile windshield to a frame by adhesive sealing means, but since assembly-belt production is generally used in automobile manufacturing plants, there is a demand for a one-liquid moisture-curable urethane sealing material composition that is capable of withstanding the stress and vibration of the frame with the movement to each process after windshield attachment,

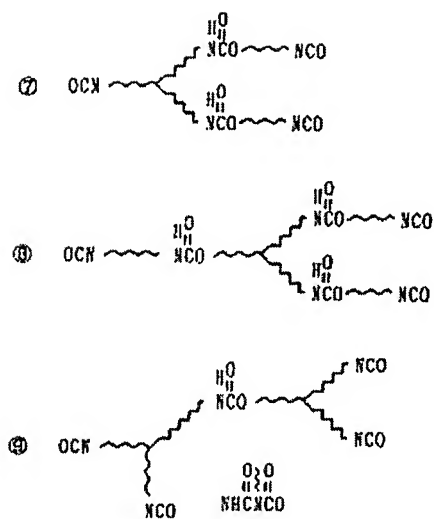
the impact of air pressure caused by the opening and closing of doors, shower tests for water leakage, and the like; has a rapid curing rate so that a good sealing effect and strong adhesion are obtained; and will not foam under high temperature or high humidity.

However, there are already sealing material compositions that satisfy these requirements, such as a moisture-curable sealing material composition containing a urethane prepolymer obtained by reacting a polyalkylene ether triol having a molecular weight of 5,000 to 8,000 and excess aromatic diisocyanate compound (refer to JP 63 [1988]-8155). This sealing material composition is fast-curing, does not foam under high temperature or high humidity, is practical and has good shelf life, and is extremely useful. However, there is a tendency toward insufficient adhesion with painted surfaces, especially when the open time (in essence, the time until bonding occurs after application of sealing material) is long (usually 5 minutes or longer); therefore, primer treatment is necessary.

Moreover, JP (Kokai) 59[1984]-78,227 describes, as a sealing material composition that takes into consideration viscosity adjustment and shelf life in particular, a moisture-curable sealing material composition comprising a prepolymer mixture consisting of urethane prepolymer (X) obtained by reacting a mixed polyol of a polyalkylene ether triol having a molecular weight of 5,000 to 7,000 and a polyalkylene ether diol having a molecular weight of 1,000 to 4,000 and excess tolylene diisocyanate and urethane prepolymer (Y) obtained by reacting the above-mentioned mixed polyol and excess diphenylmethane-4,4'-diisocyanate. This sealing material composition satisfies the previous requirements, but both of the two types of urethane prepolymers (X) and (Y) that are the primary components are obtained by reacting a specific diisocyanate

compound with a mixed polyol of polyalkylene ether triol and polyalkylene ether diol, and there is the potential for fluctuations of properties taking into consideration the possibility that a variety of products can be generated by this reaction, as shown schematically below:





, and the like.

The inventors proceeded with intensive studies to solve the problems of the prior art and as a result, successfully perfected the present invention upon discovering that a moisture-curable sealing material composition that satisfies specific requirements and solves the problems of a reduction in adhesion associated with open time and fluctuations in properties is obtained by combining two types of urethane prepolymers obtained by reaction of a specific triol component or diol component and a diisocyanate component.

### **Structure and Effect of Invention**

In essence, the present invention provides a moisture-curable sealing material composition comprising a prepolymer mixture consisting of urethane prepolymer (A) obtained by reacting a polyalkylene ether triol having a molecular weight of 4,000 to 8,000 and excess diphenylmethane-4,4'-diisocyanate (MDI hereafter), and urethane prepolymer (B) obtained by reacting a polyalkylene ether diol or polyalkylene ether triol having a molecular weight of 2,000 to 6,000 and excess tolylene diisocyanate (TDI hereafter), this moisture-curable sealing material composition characterized in that the

mixture ratio by weight of urethane prepolymer (A) and urethane prepolymer (B) is 95:5 to 70:30.

Urethane prepolymer (A) of the present invention is produced by reacting excess MDI with a polyalkylene ether triol such that, for instance, the molar ratio of NCO/OH is 1.5 to 2.5, and the free NCO content is usually set at 1.5 to 2.5 wt%. It is possible to perform the reaction using a reaction-promoting catalyst (with the amount added being 0.1 to 0.5 wt%), such as dibutyltin dilaurate, dibutyltin maleate, stannous octoate, lead octoate, or a tertiary amine.

Moreover, the resulting urethane prepolymer can be used without further treatment, but it can also be used after the residual free NCO is blocked with an active methylene compound in order to control crosslinking of the free NCO groups and the urethane bonds (allophanate bond-forming reaction) and reaction among the free NCO groups (oligomerization) and to improve shelf life. Examples of active methylene compounds are dialkyl malonates, such as dimethyl malonate, diethyl malonate, and methyl ethyl malonate, and acetoacetic acid alkyl esters, such as methyl acetoacetate and ethyl acetoacetate.

The above-mentioned polyalkylene ether triol is produced by addition polymerization of an alkylene oxide such as ethylene oxide or propylene oxide and an active hydrogen compound such as glycerin or trimethylol propane, and has a molecular weight of 4,000 to 8,000, preferably 5,000 to 7,000. If the molecular weight is less than 4,000, in terms of properties, the modulus will rise and the appropriate elongation will not be obtained, while if the molecular weight exceeds 8,000, the degree of unsaturation of the polyol will rise, there will be an increase in impurities, such as monools (there will

be a reduction in the average number of functional groups), and the desired prepolymer will not be obtained. The preferred triol is polypropylene ether triol wherein the number of ethylene oxide (EO hereafter) moles added is 20 mol% or less. If the number of EO moles added exceeds 20 mol%, there will be improved adhesion and curing rate, but there will also be a tendency toward a new generation of foaming.

Urethane prepolymer (B) of the present invention is produced by a reaction between a polyalkylene ether triol or polyalkylene ether diol and excess TDI, and as in the case of urethane prepolymer (A), the reaction is performed at an NCO/OH molar ratio of 1.5 to 2.5 and in the presence of a reaction-promoting catalyst as necessary, and the NCO content is set at 1.5 to 2.5 wt%. When the resulting prepolymer is used, it is possible to block the free NCO groups with an active methylene compound as described above.

The above-mentioned polyalkylene ether triol or polyalkylene ether diol has a molecular weight of 2,000 to 6,000, preferably 3,000 to 6,000. If the molecular weight is less than 2,000, the desired elongation will not be obtained, and if the molecular weight exceeds 6,000, there will be a considerable increase in elongation, and this will be accompanied by a tendency to not obtain the desired strength. The preferred triol or diol is polypropylene ether triol or diol wherein the number of EO moles added is 20 mol% or less.

It should be noted that although urethane prepolymer (B) is described here as being produced from a triol or a diol, these can be used alone or in combination with one another.



The moisture-curable sealing material composition of the present invention comprises a prepolymer mixture of the above-mentioned urethane prepolymer (A) and urethane prepolymer (B). The mixture ratio of urethane prepolymer (A) and urethane prepolymer (B) is selected from within a range of 95:5 to 70:30, preferably 90:10 to 80:20, by weight ratio. If the percentage of urethane prepolymer is less than 70, the curing rate will decrease, while if it is greater than 95, adhesion will be insufficient.

When necessary, appropriate amounts of other components inert to NCO can be added, including fillers (for instance, carbon black, such as furnace black or thermal black, calcium carbonate, calcined kaolin, clay, talc, and mixtures thereof); plasticizers (for instance, phthalic acid esters, such as di-2-ethylhexyl phthalate, butylhexyl phthalate, and dinonyl phthalate; benzoic acid esters, such as diethylene glycol dibenzoate and ethylene glycol monobutyl ether benzoate; partially hydrogenated terphenyl; alkyl polycyclic aromatic hydrocarbons; chlorinated paraffins; and mixtures thereof); solvents (for instance, aromatic solvents, such as toluene and xylene, esters, ketones, and ethers); and cure-promoting catalysts (for instance, tertiary amines, such as N-alkylbenzyl amine, N-alkyl morpholine, N-alkyl aliphatic polyamine, N-alkyl piperazine, trimethylene diamine, 1,8-biazacyclo[5.4.0]undecene-7, and derivatives thereof; other nitrogen-containing compounds; naphthenoic acid or octenoic acid salts of heavy metals, such as zinc, copper, lead, bismuth, cobalt, manganese, iron, and mercury; and heavy metal-containing organic compounds, such as dibutyltin dilaurate and dibutyltin maleate (with the amount added being 0.1 to 1.0 wt%)).

The composition of the present invention comprising the above-mentioned components has a rapid curing rate, does not foam, even under high temperatures and

humidity, has a low viscosity and is easily discharged, and has a good shelf life. In particular, it provides excellent adhesion with painted surfaces and plastics, even under a long open time of 10 minutes or longer, and as a result, primer treatment is omitted.

The present invention will now be described in specific terms using production examples, working examples, and comparative examples.

#### Production Example 1 (triol/MDI)

3,000 g of polyoxypropylene ethylene triol having a molecular weight of 7,000 (number of EO moles = 15 mol%) were introduced into a nitrogen-purged reactor, reduced-pressure drying was performed under vacuum pressure (10 mmHg or less; the same hereafter), the water content of the reactants was confirmed to be 0.05% (wt%; the same hereafter) or less; then MDI was added (370 g); and the mixture was stirred for 30 minutes under vacuum while bringing the temperature to  $80 \pm 5^{\circ}\text{C}$ . 30 minutes later, the reactants were returned to normal pressure with nitrogen gas, a 1% toluene solution of dibutyltin dilaurate (1 g) was added, and the reaction was again performed under vacuum pressure for four hours ( $80 \pm 5^{\circ}\text{C}$ ). After the reaction, the product was cooled to obtain a urethane prepolymer having a free NCO content of 2.2% and a viscosity of 45,000 cps/ $20^{\circ}\text{C}$ .

#### Production Example 2 (triol + diol/MDI)

2,000 g of polyoxypropylene ethylene triol having a molecular weight of 7,000 (number of EO moles = 15 mol%) were introduced into a nitrogen-purged reactor; 1,000 g of polyoxypropylene diol having a molecular weight of 3,000 (number of EO moles = 0 mol%) were added; then MDI were added (429 g); and the reaction was performed by the

same procedure as in Production Example 1, and a urethane prepolymer having a free NCO content of 2.3% and a viscosity of 55,000 cps/20°C was obtained.

#### Production Example 3 (triol/TDI)

3,000 g of polyoxypropylene triol having a molecular weight of 5,000 (number of EO moles = 10 mol%) were introduced into a nitrogen-purged reactor, then TDI (mixture of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate, the same hereafter, 293 g) was added and the reaction was performed by the same procedure as in Working Example 1, and a urethane prepolymer having a free NCO content of 2.1% and a viscosity of 11,000 cps/20°C was obtained.

#### Production Example 4 (diol/TDI)

3,000 g of polyoxypropylene diol having a molecular weight of 3,000 (number of EO moles = 0 mol%) were introduced into a nitrogen-purged reactor, then TDI (298 g) was added and the reaction was performed by the same procedure as in Production Example 1, and a urethane prepolymer having a free NCO content of 2.0% and a viscosity of 15,000 cps/20°C was obtained.

#### Production Example 5 (triol + diol/TDI)

2,000 g of polyoxypropylene triol having a molecular weight of 5,000 (number of EO moles = 10 mol%) and 1,000 g of polyoxypropylene diol having a molecular weight of 3,000 (number of EO moles = 0 mol%) were introduced into a nitrogen-purged reactor, then TDI (316 g) was added and the reaction was performed by the same procedure as in Production Example 1, and a urethane prepolymer having a free NCO content of 2.3% and a viscosity of 16,000 cps/20°C was obtained.

#### Working Examples 1 through 4 and Comparative Examples 1 through 7

450 g of a mixture, which was obtained by mixing, by the number of parts shown in the following Table 1, the urethane prepolymers obtained in Production Examples 1 through 5 were introduced into a nitrogen-purged stirring vessel, and then 300 g of dehydrated di-2-ethylhexyl phthalate were introduced. The components were stirred together under a nitrogen atmosphere, and then 550 g of dry carbon black and 300 g of dry calcium carbonate were gradually added. Once addition was completed, the mixture was defoamed and stirred for 30 minutes under vacuum pressure (10 mmHg or less). Then 80 g of xylene for adjusting viscosity and 0.5 g of a cure-promoting catalyst, dibutyltin dilaurate, were introduced and the mixture was stirred for 10 minutes under vacuum pressure. The resulting sealing material composition was transferred to an airtight aluminum cartridge. The properties of the sealing material are shown in Table 1.

Table 1

		Working Examples					Comparative Examples						
		1	2	3	4		1	2	3	4	5	6	7
Urethane prepolymer	Production Example 1	10	10	10	10		10	-	10	10	10	-	-
	Production Example 2	-	-	-	-		-	10	-	-	-	10	10
	Production Example 3	1	2	-	-		-	-	5	-	-	5	-
	Production Example 4	-	-	1	2		-	-	-	5	-	-	5
	Production Example 5	-	-	-	-		-	-	-	-	5	-	-
	Appearance	Black paste	Black paste	Black paste	Black paste		Black paste	Black paste	Black paste	Black paste	Black paste	Black paste	Black paste
Viscosity (MCM)		75	73	78	74		85	88	71	68	73	69	71
Curing rate (minutes)		43	47	44	47		40	41	58	59	60	58	61
Open time (minutes)		10	11	10	10		6	6	14	15	14	13	14
Elongation (%)		525	550	575	600		500	525	525	650	575	550	650
Tensile strength (kg/cm <sup>2</sup> )		60.5	62.5	59.5	61.5		62	60	40.4	41.8	45.3	48.5	41.5
Hardness		52	53	54	51		54	55	50	44	49	49	44
Shelf life		Good	Good	Good	Good		Good	Good	Good	Good	Good	Good	Good

Note) The test methods were as follow:

- (1) Appearance: Macroscopic
- (2) Viscosity: Measured at 25°C using a MacMichael viscosimeter.
- (3) Curing rate: Tack-free time at 20°C and 65% relative humidity.
- (4) Open time: Critical open time (minutes) within which it is possible to obtain good painted surface adhesion under 95% relative humidity.
- (5) Elongation, tensile strength, hardness: Measured in accordance with JIS K-6301<sup>\*</sup> after being cured for 7 days under conditions of 20°C and 65% relative humidity.
- (6) Shelf life: Observation of state after being stored for 30 days at 40°C under an airtight seal.

According to the results in Table 1, the sealing material compositions of Working Examples 1 through 4 all were good in terms of the test items, but the open time was too short in Comparative Examples 1 and 2, and the curing rate was slow and there was a reduction in tensile strength in Comparative Examples 3 through 7.

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<sup>\*</sup> Japanese Industrial Standard—Trans. note.